Theory for two-photon photoemission: transport and temperature effects

R. Knorren*, G. Bouzerar, and K. H. Bennemann
Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany
(February 1, 2008)

Using a theory which treats on equal footing transport of excited electrons and electron-phonon scattering, we are able to explain the temperature dependence of the relaxation time in Cu as recently observed by Petek, Nagano, and Ogawa. We show that the unexpected increase of the relaxation time with temperature results from the drastic change of the electron motion due to the efficiency of electron-phonon scattering: the transport is ballistic at low temperature and gets diffusive at room temperature. Finally, our theory also reproduces the experimental measurements of the two-photon photoemission (2PPE) intensity as a function of the pump-probe delay.

Due to advances in the ultrashort laser techniques, very efficient tools to study the dynamics of excited electrons in semiconductors and metals are available. One of the key methods is the time-resolved two-photon photoemission (TR 2PPE) which has the crucial advantage to allow a direct measurement of the variation of the electron distribution.[1–6] Recent measurements on Cu have shown an unusual non-monotonic behavior of the relaxation time as a function of energy.[7–10] Furthermore, an unexpected increase of the relaxation time with temperature was reported.[11] We have recently developed a theory for the dynamics of excited electrons in metals, which explicitly includes the effect of secondary electrons,[12–14] in contrast to *ab-initio* calculations of the electronic lifetime.[15–18] It consists in solving a Boltzmann-type equation in the random-**k** approximation. Within our approach, we were able to reproduce the peak in the relaxation time at the right energy and a linear shift with photon frequency, in agreement with experiments. We have also analyzed in detail the structure and height of the peak and the role of secondary electrons, especially focussing on the Auger contribution and the *d*-hole lifetime.

To explain the observed temperature dependence, in this paper we extend our model by including effects of transport of excited electrons out of the detection region and electron-phonon scattering. Note that the temperature dependence of the relaxation time is striking, since on the basis of Fermi-liquid theory (FLT) one would expect only a very small *decrease* of $\tau(E,T) = a_0/[(E-E_F)^2 + b(k_BT)^2]$.[19,20] Since b is of oder 1 and k_BT is much smaller than $E-E_F$, the reduction is insignificant for excited electrons of energy of order 1 eV. But if one assumes that electron-phonon collisions are efficient enough to change the nature of the transport from a regime almost ballistic at low temperature to a diffusive regime at room temperature, then one should expect a longer relaxation time at higher temperature. This is supported by the observation that ballistic transport strongly reduces the relaxation time.[3,9,13]

Let us now describe the theoretical approach we use. The temporal variation of the occupation of a level of energy E and momentum $\mathbf{k}$ at distance z from the surface is described by a Boltzmann-type equation:

$$\frac{\partial f(E,\mathbf{k},z)}{\partial t} = \left[\frac{\partial f}{\partial t}\right]_{opt} + \left[\frac{\partial f}{\partial t}\right]_{e-e} + \left[\frac{\partial f}{\partial t}\right]_{transp} + \left[\frac{\partial f}{\partial t}\right]_{e-ph} , \qquad (1)$$

where respectively the first term corresponds to the optical excitation, the second one describes the electron-electron scattering, the third is the ballistic transport and the fourth is the electron-phonon scattering. The transport term is given by[21]

$$\left[\frac{\partial f}{\partial t}\right]_{transp} = -v_z \frac{\partial f}{\partial z} . \qquad (2)$$

Here, v_z is the z-component of the electron velocity. We only consider transport in the z-direction, because the diameter of the laser spot is much larger than the optical penetration depth. Detailed expressions for $\left[\frac{\partial f}{\partial t}\right]_{e-e}$ in the random-**k** approximation (including secondary-electron generation) and for the optical excitation term $\left[\frac{\partial f}{\partial t}\right]_{opt}$ are given in Ref. 13. To derive the electron-phonon scattering term, we first consider the general expression,[22,23] neglecting the transfer of energy to the lattice. The exchange of energy between the lattice and the hot electrons starts to get really effective only after 0.5 ps,[24,25] which is not the regime we consider here. Also, in noble metals there is only one acoustic branch (1 atom/unit cell), and an upper bound for the phonon-energy average is $\hbar\langle\omega_{ph}\rangle \approx k_BT_D$, where T_D is the Debye temperature. For Cu $\hbar\langle\omega_{ph}\rangle \approx 20$ meV,[26] which can be neglected since it is small enough compared to the excited-electron energy (≈ 1 eV). On the other hand, large transfer of momentum is allowed, since the Debye cut-off is of order $k_Da \approx \pi$ (a is the lattice spacing).[27] This is a crucial point in our theory, because only large momentum transfer will efficiently change the direction of propagation of the electrons. Let us then express within these simplifications, the electron-phonon scattering contribution in the random-**k** approximation:

$$\left[\frac{\partial f(E,\mathbf{k})}{\partial t}\right]_{e-ph} = -\Gamma \int \frac{d\Omega_{\mathbf{k}'}}{4\pi}[1-f(E,\mathbf{k}')]f(E,\mathbf{k}) + \Gamma \int \frac{d\Omega_{\mathbf{k}'}}{4\pi} f(E,\mathbf{k}')[1-f(E,\mathbf{k})] \ , \quad (3)$$

where $\Gamma = \frac{2\pi}{\hbar}|g|^2(2\langle n\rangle + 1)\rho(E_F)$ is the electron-phonon scattering rate. $\rho(E_F)$ is the density of states at the Fermi surface, $\Omega_{\mathbf{k}'}$ denotes the solid angle, and $\langle n\rangle = \{\exp[\hbar\langle\omega_{ph}\rangle/(k_BT)] - 1\}^{-1}$ denotes the thermal average of the phonon occupation. Additionally we assume that the coupling function g is constant. Noticing that $k_BT \gg \hbar\langle\omega_{ph}\rangle$, we get the well-known formula

$$\Gamma = \frac{2\pi}{\hbar}\lambda k_B T \ , \quad (4)$$

where $\lambda = 2|g|^2\rho(E_f)/(\hbar\langle\omega_{ph}\rangle)$ is the so-called electron-phonon mass enhancement factor.[22] The last step in evaluating Eq. (3) is to make the substitutions $f(E,\mathbf{k}) \to f(E,v)$, where v is the z-component of the velocity, and $\int \frac{d\Omega_{\mathbf{k}'}}{4\pi}[1-f(E,\mathbf{k}')] \to \frac{1}{N}\sum_j [1-f(E,v_j)]$.

The 2PPE intensity is calculated as the convolution of the probe laser intensity $P(t)$ with the distribution of excited electrons in the vicinity of the surface:[13]

$$I^{\rm 2PPE}(E,\Delta t) = \int_{-\infty}^{\infty} dt\ P(t-\Delta t) \times \int_0^{\infty} dz\ e^{-z/\lambda_{\rm esc}} f(E,z,t) \ , \quad (5)$$

where $\lambda_{\rm esc} = 1.6$ nm is the escape depth taken from overlayer experiments.[28] The effective relaxation time τ is extracted from the 2PPE intensity as a function of pump-probe delay, as in experiments.

In order to allow a direct comparison between our calculations and the available experimental data we also use in the calculations a laser pulse of duration 12 fs and energy 3.1 eV. For Cu, we use 15 nm for the optical penetration depth and $v_t = 1.8$ nm/fs for the transport velocity. We chose $\tau_h = 35$ fs for the d-hole lifetime, since it was shown in a previous study that this provides a good order of magnitude for the height of the peak in the relaxation time in Cu.[14] This is also in agreement with two independent experimental measurements which have suggested a lower bound of order 25 fs.[29,30] We have no other free parameter, since the parameter λ which enters in the electron-phonon scattering rate Γ was measured to be $\lambda \approx 0.15$.[22,31] Note, by using Eq. (4) one can already get an insight of the effect of the electron-phonon collisions on the transport: at $T = 300$ K the average time between two elastic collisions is $\tau_{e-ph} = 1/\Gamma \approx 30$ fs, in agreement with the value extracted from resistivity measurements ($\tau_{e-ph} = 27$ fs).[32] However, at $T = 50$ K, we get $\tau_{e-ph} \approx 170$ fs. Thus, since an excited electron at 1 eV has a relaxation time of order $\tau_e = 50$ fs, one expects almost no effect on transport due to electron-phonon scattering at $T = 50$ K, because $\tau_{e-ph} \gg \tau_e$. In contrast, at $T = 300$ K, one has $\tau_{e-ph} \le \tau_e$, and thus the phonons will be very effective in changing the nature of the transport.

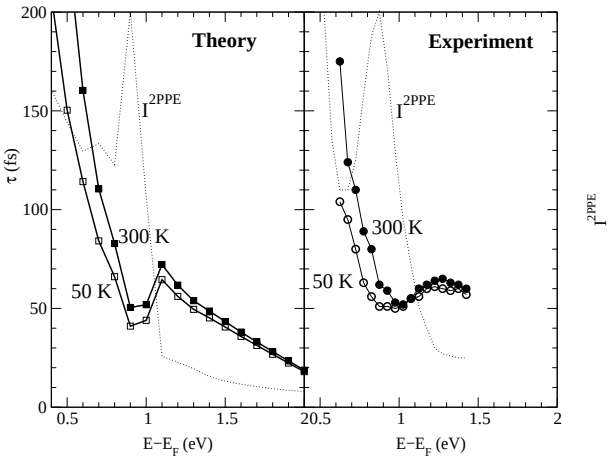

FIG. 1. Temperature dependence of the relaxation time τ (experimental data for Cu(111) from Ref.[11]). The dotted line shows the 2PPE spectrum $I^{\rm 2PPE}(\Delta t = 0)$ in arbitrary units. The pulse duration is 12 fs and the photon energy 3.1 eV.

In Fig. 1 we have plotted both the 2PPE intensity $I^{\rm 2PPE}(\Delta t = 0)$ and the relaxation time τ at $T = 300$ K and $T = 50$ K as a function of energy. We compare our results with the experimental data of Ref. 11. First, the 2PPE intensity in both theoretical and experimental data compare quite well. A pronounced peak due to transitions from the d band appears at $E - E_F = 0.9$ eV and is followed by a sharp threshold at around 1.1 eV. At low energy, we again observe an increase of the 2PPE signal. Second, the data for the relaxation time show a surprisingly good agreement: i) the positions of the peak and the dip in the relaxation time are identical; ii) the structure is similar, although the height of the peak is larger in our calculation, which could indicate that the d-hole lifetime τ_h could be smaller than the value of 35 fs considered here; iii) the magnitude of the change due to the temperature is the same. For example, at $E = 0.6$ eV and 300 K we get for both the experimental and calculated relaxation time $\tau_{exp} = 175$ fs and $\tau_{th} = 170$ fs, while at 50 K we find $\tau_{exp} = 105$ fs and $\tau_{th} = 110$ fs. This agreement is surprisingly good. As expected at sufficiently high energy $E - E_F > 1.5$ eV the relaxation time is almost unaffected, since the excited-electron lifetime is smaller in both cases than τ_{e-ph}.

In Fig. 2 we compare the 2PPE intensity as a function of the pump-probe delay with the data from Ref. 11. One can observe a strong temperature dependence, especially at low energy. Again we get very good agreement for both the quantitative and qualitative aspects. Note that the experimental results include a peak at $\Delta t = 0$, which is absent in the calculations because our theory does not include coherent effects. So one should compare the data for $\Delta t < -20$ fs. First, at low energy up to 0.7 eV, in both cases a clear delayed rise is observed at $T = 300$ K.

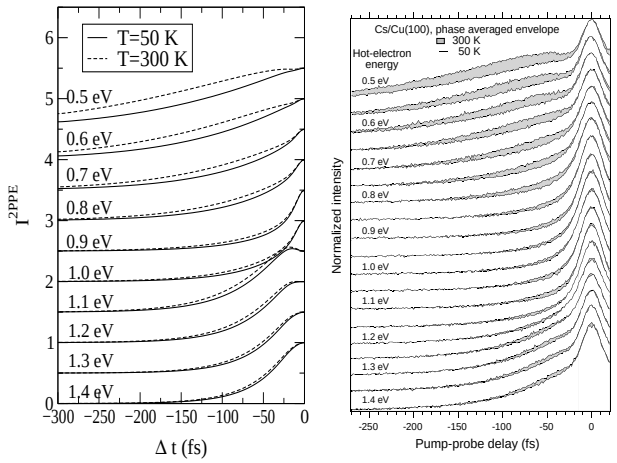

FIG. 2. Temperature dependence of the 2PPE intensity for different energies $E - E_F$ as a function of pump-probe delay. The data on the right side are experimental results from Ref.[11] The data on the left side are the theoretical results. Note the delayed rise at low energy for $T = 300$ K which leads to the larger relaxation time.

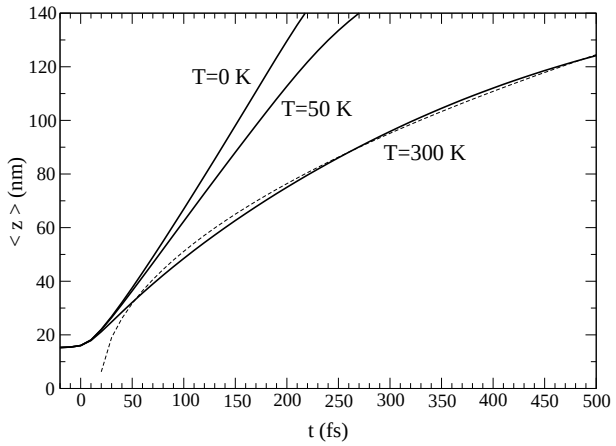

FIG. 3. Average distance $\langle z \rangle$ of excited electrons from the surface after laser excitation. Note that at $T = 0$ and 50 K the transport is ballistic, while at $T = 300$ K it is diffusive due to elastic electron-phonon collisions. The dashed line is a fit using $\langle z \rangle = \sqrt{D(t - t_0)}$.

Second, the magnitude of the temperature effect agrees surprisingly well with the experimental data. It is more pronounced at low energy and decreases with increasing energy. In a very small window of energy around 1.1 eV (just above the d-band threshold), we observe a reappearance of the delayed peak accompanied by a slight new increase of the temperature dependence. The increase at 1.1 eV was also noted in Ref. 11, although the delayed rise seems to be absent. It is also interesting to remark that such a rise could be observed for the first time, since a sufficiently short laser pulse was used. This rise is in fact a signature of the presence of secondary electrons.

To illustrate the reason why the effect of temperature is so strong, let us analyze the motion of the excited-electron distribution as a function of time. As a measure for the penetration of electrons into the bulk, we define the average distance from the surface, $\langle z(t) \rangle$:

$$\langle z(t) \rangle = \frac{\int_0^\infty dz z N(z,t)}{\int_0^\infty dz N(z,t)} , \qquad (6)$$

where $N(z,t) = \int_0^\infty dE \rho(E) f(E,z,t)$ is the average number of excited electrons at distance z and time t. In Fig. 3, we have plotted $\langle z(t) \rangle$ at different temperatures, $T = 0$, 50, and 300 K. Clearly we observe that at $T = 0$ and 50 K, the motion of the excited electrons is ballistic. At $T = 50$ K, a small deviation from the linear behavior appears around $t \approx 200$ fs, which is of the order of magnitude of $\tau_{e-ph} = 170$ fs. We get for the average velocity $\Delta\langle z \rangle / \Delta t \approx v_t/2$, where the factor 1/2 can be understood easily by considering the average of the velocity in z direction. However, the nature of the motion has drastically changed at $T = 300$ K: the motion is now diffusive. We illustrate this by fitting the data with $\langle z \rangle = \sqrt{D(t - t_0)}$, which is expected in the case of diffusive motion. An offset t_0 is introduced in order to take into account the finite duration of the laser pulse generating excited electrons. We get $D = 32$ nm^2/fs, which agrees very well with the expression for the electronic diffusion coefficient $D = v_t l_e/3 = 29$ nm^2/fs, where $l_e = v_t \tau_{e-ph}$ is the electronic mean free path. It is interesting to note that at $t = 0.5$ ps the excited electrons have already reached an average distance of 120 nm, about ten times larger than the optical penetration depth. This is in agreement with a value of 100 nm used to describe the initial spatial distribution of excited electrons in the two-temperature model.[33] Such a model does not describe the thermalization of the electron gas and starts to be valid only after $t \geq 0.5$ ps. Thus, one has to add $\langle z(t = 0.5 \text{ ps}) \rangle$ to the optical penetration depth.

To conclude, we have presented a theoretical model including both transport and electron-phonon scattering which is able to reproduce the temperature dependence of the relaxation time. It is shown that this variation is due to a drastic change of the excited-electron motion, which is ballistic at low temperature and gets diffusive at room temperature. Note that the correct order of magnitude of the temperature effect is obtained without using free parameters: the electron-phonon scattering rate was directly taken from experimental data. Furthermore, we also observe at low energy a delayed rise in the 2PPE intensity and an increase due to temperature in agreement with the experimental results. As a final remark, we have provided a very efficient method to describe the excited-electron dynamics in the short-time regime, where electron-phonon energy transfer is negligible (below ≈ 0.5 ps). The results obtained here indicate that it is promising to use our extended model to study other

problems, in particular the dynamics of excited electrons involving transport effects in the regime where electron-lattice energy transfer becomes relevant. So far, the only method available for this purpose is the two-temperature model, which is not always reliable.[34] The present theory is also suitable for the study of thin films, which offer the possibility to probe the effect of transport. Our paper shows how new information about the dynamics of excited electrons in solids can be extracted from 2PPE.

We would like to thank H. Petek, M. Aeschlimann, E. Matthias, and H. C. Siegmann for interesting discussions and helpful comments. Financial support by Deutsche Forschungsgemeinschaft, Sfb 290 and 450, is gratefully acknowledged.

---

* Author to whom correspondence should be addressed. Electronic mail can be sent to knorren@physik.fu-berlin.de or bouzerar@physik.fu-berlin.de

[1] C. A. Schmuttenmaer, M. Aeschlimann, H.E. Elsayed-Ali, R.J.D. Miller, D.A. Mantell, J.Cao, and Y. Gao, Phys. Rev. B **50**, 8957 (1994).
[2] T. Hertel, E. Knoesel, M. Wolf, and G. Ertl, Phys. Rev. Lett. **76**, 535 (1996).
[3] M. Aeschlimann, M. Bauer, and S. Pawlik, Chem. Phys. **205**, 127 (1996).
[4] S. Ogawa, H. Nagano, and H. Petek, Phys. Rev. B **55**, 10869 (1997).
[5] M. Aeschlimann, M. Bauer, S. Pawlik, W. Weber, R. Burgermeister, D. Oberli, and H.C. Siegmann, PRL **79**, 5158 (1997).
[6] J. Cao, Y. Gao, H.E. Elsayed-Ali, R.J.D. Miller, D.A. Mantell, Phys. Rev. B **58**, 10948 (1998).
[7] S. Pawlik, M. Bauer and M. Aeschlimann, Surf. Sci. **377-379**, 206 (1997).
[8] J. Cao, Y. Gao, R.J.D. Miller, H.E. Elsayed-Ali, and D.A. Mantell, Phys. Rev. B **56**, 1099 (1997).
[9] E. Knoesel, A. Hotzel, and M. Wolf, Phys. Rev. B **57**, 12812 (1998).
[10] H. Petek, H. Nagano, M.J. Weida, and S. Ogawa, Chem. Phys. **251**, 71 (2000).
[11] H. Petek, H. Nagano, and S. Ogawa, Appl. Phys. B **68**, 369 (1999).
[12] R. Knorren and K.H. Bennemann, Appl. Phys. B **68**, 401 (1999).
[13] R. Knorren, K. H. Bennemann, R. Burgermeister, and M. Aeschlimann, Phys. Rev. B **61**, to appear, and cond-mat/9910326
[14] R. Knorren, G. Bouzerar, and K. H. Bennemann, cond-mat/0002293 and submitted to Phys. Rev. B
[15] I. Campillo, J.M. Pitarke, A. Rubio, E. Zarate, and P.M. Echenique, Phys. Rev. Lett. **83**, 2230 (1999).
[16] P.M. Echenique, J.M. Pitarke, E.V. Chulkov, and A. Rubio, Chem. Phys. **251**, 1 (2000).
[17] W.D. Schöne, R. Keyling, M. Bandić, and W. Ekardt, Phys. Rev. B **60**, 8616 (1999).
[18] R. Keyling, W.D. Schöne, and W. Ekardt, Phys. Rev. B **61**, 1670 (2000).
[19] J.J. Quinn, Phys. Rev. **126**, 1453 (1962).
[20] D. Pines and P. Nozières, *The Theory of Quantum Liquids* (Benjamin, New York, 1966).
[21] J.M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, 1972).
[22] G. Grimvall, *The electron–phonon interaction in metals*, in *Selected topics in solid state physics*, edited by E.P. Wohlfahrt, Vol. 16, (North Holland, 1981).
[23] P. B. Allen, Phys. Rev. Lett. **59**, 1460(1987).
[24] C. Suarez, W.E. Bron, and T. Juhasz, Phys. Rev. Lett. **75**, 4536 (1995).
[25] W.S. Fann, R. Storz, H.W.K Tom, J. Bokor, Phys. Rev. B **46**, B 13592 (1992).
[26] S. D. Brorson, A. Kazeroonian, J. S. Moodera, D. W. Face, T. K. Cheng, E. P. Ippen, M. S. Dresselhaus, and G. Dresselhaus, Phys. Rev. Lett. **64**, 2172 (1990).
[27] N. D. Ashcroft, N. D. Mermin, *Solid State Physics* (Saunders College, 1976).
[28] H. C. Siegmann, Surf. Sci. **307-309** 1076 (1994).
[29] R. Matzdorf, A. Gerlach, F. Theilmann, G. Meister, A. Goldmann, Appl. Phys. B **68**, 393 (1999).
[30] H. Petek, H. Nagano, and S. Ogawa: Phys. Rev. Lett. **83**, 832 (1999).
[31] B. A. McDougall, T. Balasubramanian, and E. Jensen, Phys. Rev. B **51**, 13 891 (1995).
[32] G.W.C. Kaye and T.H. Laby, *Table of Physical and Chemical Constants* (Longmans Green, London, 1966)
[33] J. Hohlfeld, S.S. Wellershoff, J. Güdde, U. Conrad, V. Jähnke, and E. Matthias, Chem. Phys. **251**, 237 (2000).
[34] R. H. M. Groeneveld, R. Sprik, and A. Lagendijk, Phys. Rev. B **51**, 11 433 (1995).